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Technical Report No. 131

An Electrochemical and Spectroelectrochemical Study of Substituted
Alkylidenecyclopropabenzene. 1-(Diphenylmethylene)cyclopropabenzene in
the First Anodic and Cathodic Voltammetric Waves in Acetonitrile

by

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¹These half-wave potentials were obtained from refs. 5, 10, and 11, assuming where necessary that the potential of the Ag/Ag⁺ reference electrode is 0.3 V more positive than that of the saturated calomel electrode

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An electrochemical and spectroelectrochemical study of substituted alkylidenecyclopropabenzene: 1-(diphenylmethylene)cyclopropabenzene in the first anodic and cathodic voltammetric waves in acetonitrile

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[Traduit par le Centre de Recherches]

Introduction

The unusual properties and reactivity of highly strained molecules have interested chemists for quite some time (1). Presently there is a great deal of interest and research activity in cyclopropene chemistry. Cyclopropenes possess some of the highest strain energies known (2); the parent compound **I** has a strain energy of 68 kcal/mol (3). As a result, the electrochemical oxidation and reduction potentials of the neutral molecules are lower than those of most other electroactive hydrocarbons.

Even more highly strained and unusual alkylidene derivatives of **I** have been reported (4): the diphenylmethylene (**III**) and the 1-phenylethylidene (**IV**) derivatives have been synthesized, as well as the corresponding naphthalene analogs **V** and **VI**. Compounds **III** and **V** are stable in air and in aprotic solvents against rapid oxidation. The methylenecyclopropene parent

compound **II** has not been successfully isolated, but attempts to synthesize this species continue.

The possibility of charge separated resonance forms contributing to the stability of the neutral molecule **V** was suggested by an initial spectral characterization. We have recently reported the results of an electrochemical and spectroelectrochemical study of **V** (5), and in an effort to further characterize and understand the nature of the special properties of these molecules we have undertaken an electrochemical and spectroelectrochemical investigation of **III**. One question is how large a role does the aromatic moiety of the cyclopropene ring play in the stability of the ion radicals compared to the substituents on the methylene group. The naphthalene analog in the previous study was shown to form a stable anion radical (on the timescale of the experiment) when electrochemically reduced in oxygen-free acetonitrile solution. When oxygen is present the anion radical reacts rapidly with O_2 at a rate approaching the diffusion limit. Additionally, the compound was shown to form a quasi stable cation radical when electrooxidized. In the present study, compound **III** has been found to behave similarly. In addition, the homogeneous rate constant for the decay of the cation radical in acetonitrile solution has been computed from spectroelectrochemical transient data.

Experimental

Chemicals and reagents

The preparation of **III** has been described in detail (4, 14). A stirred solution of cyclopropabenzene in dry THF was cooled to -70°C under oxygen-free nitrogen; *n*-butyllithium in hexane was added slowly, while the bath temperature was allowed to rise to -40°C . After 1.5 h the solution was again cooled to -70°C , and trimethylsilyl chloride was added dropwise until the deep orange solution had become colorless. The reaction mixture was allowed to warm slightly for 1 h and then cooled again to -70°C , at which time the above metallation procedure with *n*-butyllithium was repeated. Quenching of the generated α -silyl carbanion was attained with benzophenone in THF, and the resulting clear yellow solution was allowed to warm to room temperature. After 1.5 h aqueous sodium bicarbonate was added after which the mixture was extracted with dichloromethane. The combined organic extracts were washed with water, dried with magnesium sulfate, and concentrated to an orange oil under reduced pressure. This oil was then passed through a silica gel column (petroleum ether:ethyl acetate, 9:1) and fractions of the most mobile component, 1-(diphenylmethylene)cyclopropabenzene, were collected as a yellow oil which solidified on standing at -20°C . Recrystallization from petroleum ether gave yellow needle-like crystals, mp $89-91^\circ\text{C}$.

The preparation of tetra-*n*-butylammonium tetrafluoroborate (TBAF) has been described previously (6). This supporting electrolyte was prepared from the metathesis of sodium tetrafluoroborate and tetra-*n*-butylammonium hydrogen sulfate. The crude product was washed with ice water, dissolved in a minimum amount of methylene chloride, and precipitated with cold diethyl ether. After a second recrystallization, the product was air dried and stored in a vacuum oven at 75°C for 24 h before use.

Acetonitrile was hplc grade (Baker Chemicals, 0.001% nominal water content) and was used as received. Deoxygenation of the reaction mixture was accomplished by purging with dry helium gas immediately prior to the experiments.

The reference electrode was a silver wire immersed in 0.01 M silver nitrate and 0.10 M TBAF in acetonitrile. We report all potentials with respect to this reference.

Electrochemistry and spectroelectrochemistry

A three electrode potentiostat and a waveform generator (JAS Instrument Systems, Inc.) provided the control of electrode potential. Cyclic voltammetry was conducted in a three-electrode kinetic cell wherein a platinum wire working electrode surrounded by a cylindrical platinum foil secondary electrode was mounted. A Luggin capillary reference electrode tip was situated within about 1 mm of the working electrode. Although the geometry of the setup is cylindrical, the experiments were carried out on a timescale where linear diffusion is observed. See ref. 7 for precise details. For spectroelectrochemical experiments, a cell was used that held a 7 mm diameter platinum mirror disk working electrode with a planar Pt foil counter electrode situated opposite, providing good linear diffusion characteristics for up to 10 s. Two quartz windows were mounted to enable passage of incoming and outgoing uv/vis radiation at a 45° angle of incidence and reflection. A Luggin reference probe was positioned close to the working electrode so as not to obstruct the optical path. Exact details have been described previously (8).

The spectroelectrochemical cell was mounted on an optical bench, and the optical beam from a monochromator (GCA McPherson model 302) was directed onto the electrode surface, and reflected onto a photomultiplier tube (RCA model 31000A). The signal from the PMT was digitized by an oscilloscope (Tektronix model 5223); this datum was transmitted over a GPIB interface to a computer (IBM PC/AT). The computer signal averaged digitized data from single reflectance transients; the background intensity was controlled so that the value of the relative reflectance could be calculated as described in ref. 8. The MSRS technique used in this work was implemented by first maintaining the potential at a value where no electrochemical reaction occurred. The potential was then stepped to a value where electro-



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oxidation or electroreduction was forced into diffusion control, and the spectroelectrochemical reflectance transient response of the electrogenerated species was recorded on the digitizing oscilloscope as a function of time after the potential pulse was applied. Alternately, the potential was also modulated at a high frequency (40 Hz) and the resulting ac reflectance change monitored with a lock-in amplifier. Scanning wavelength simultaneously provided uv-vis difference spectra of the reactants, intermediates, and products (8).

Results and discussion

Voltammetry

A. Anions

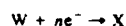
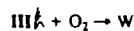
At a platinum electrode, the voltammetric reduction of a blank solution containing only supporting electrolyte showed no faradaic current ($<0.1 \mu\text{A cm}^{-2}$) over the range of potentials studied. Cyclic voltammetry of **III** at negative potentials in oxygen-free acetonitrile solution is shown in Fig. 1a. A one-electron wave due to the reduction of the neutral molecule to the anion radical at the platinum working electrode is observed. The voltammetric response indicates electrochemical reversibility at this (50 mV s^{-1}) and faster sweep rates: the voltammetric peak separation is 60 mV, and the ratio of cathodic to anodic peak currents is unity. The half-wave potential is $-2.32 \text{ V vs. Ag/Ag}^+$. There is no evidence of anion radical decay on the experimental timescale (ca. 1 min); the anion radical is quite stable, as is that of the naphthyl cyclopropane analog (5).

When only oxygen is present in solution a voltammogram such as that in Fig. 1b results. The first cathodic wave at $-1.60 \text{ V vs. Ag/Ag}^+$ corresponds to the reduction of oxygen to superoxide, which is a kinetically slow electron transfer (5). On the return excursion an anodic peak at -0.78 V due to the reoxidation of superoxide is seen. The diffusion-controlled peak for the formation of superoxide is thus 750 mV less negative than the peak potential for the formation of the anion radical of **III** at a sweep rate of 50 mV/s . (At glassy carbon the reduction of oxygen is kinetically more reversible: the separation between the cathodic peak due to the formation of superoxide and the corresponding oxidation peak is reduced from about 820 mV at platinum at 240 mV on carbon at these sweep rates.)

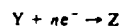
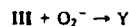
Plots of cathodic peak current versus square root of sweep rate for both dioxygen and isolated **III** are linear for sweep rates of up to 500 mV/s ; the plots intersect the origin. This is the expected result for an electrochemical reaction where there are no complicating side reactions involving reactants or products, and where there are no complications due to adsorption of species undergoing electron transfer. Uncomplicated electrochemical formation of the anion radical of **III** and of superoxide is thus consistent with observations; both reductions are simple one-electron transfers.

However, solutions containing both **III** and oxygen demonstrate more complicated voltammetry than that of the individual systems described above (Fig. 2). As in Fig. 1, the first reduction wave at -1.60 V corresponds to the formation of superoxide. We observe, however, that the magnitude of the current in the second wave at -2.35 V , due to the formation of the anion radical of **III** is larger than that for the simple one electron transfer as was observed in the single component **III** system. There are several possible explanations for this behavior.

One possibility is the case where an electroactive product is formed whose reduction potential is less negative than that of **III**. In the present case, this would most likely be due to the reaction of the anion radical of **III** with diffusing oxygen or superoxide:



or

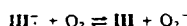


(The second reaction is unlikely, as it is unfavorable energetically.) However, bulk electrolysis of **III** at potentials up to and less negative than -2.35 V yielded no evidence of the expected products of either of the proposed reaction schemes. Additionally, if such an electron transfer — chemical step — electron transfer scheme were indeed occurring, the height of the second cathodic wave would imply the involvement of more than one electron in the reduction of W or Y which, though possible, is unlikely.

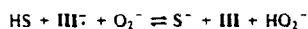
Voltammetric experiments revealed no evidence of the reaction of unreduced **III** with oxygen. Upon deoxygenation with helium purging of the mixed (both **III** and O_2 present) solution, the uncomplicated electrochemical behavior shown in Fig. 1a could be reproduced. Also, if in the mixed system,

a cyclic voltammogram was run to a switching potential past the peak for oxygen reduction but prior to the cathodic wave corresponding to reduction of **III**, the reverse sweep yielded an oxidation peak for superoxide which was uncomplicated, as per Fig. 1b. This is evidence that superoxide does not react chemically to any appreciable extent with **III**, although Fig. 2 shows a depletion of available total radical anion of **III** in the diffusion layer; the oxidation peak at -2.29 V is reduced in magnitude when O_2 is present. All of the above possibilities suggest that a product of the addition of **III** and oxygen should be observed, but exhaustive electrolyses at or beyond the second reduction wave gave no significant yields of any product of **III** except the anion radical.

Another possible explanation for the unusually high current seen in the second reduction wave (in the mixed system) is the catalytic regeneration of **III** by reaction of oxygen with the anion radical to form **III** and superoxide:



In turn, superoxide reacts with the anion radical to form **III** and peroxide in the presence of a proton donor:



Whereas O_2^- is not a strong enough base to react with HS in dry acetonitrile (O_2^- is stable in dry acetonitrile for about 40 min), electron transfer from III^{*-} to O_2^- would form a base (5) such as O_2^{2-} that is now strong enough to react with HS (the solvent). These results imply that electrochemical reduction of superoxide to peroxide is thermodynamically feasible at potentials where **III** is reduced, but that the electrode reaction is very slow. The formation of peroxide in acetonitrile has been previously observed (9), where superoxide in the presence of any available proton donor was reported to disproportionate to peroxide and oxygen. Bulk electrolysis of the mixed system at a potential of -2.40 V did indeed give rise to solutions which were found to contain peroxide ion, as evidenced by testing with Fenton's reagent. Thus, if **III** is regenerated continuously in the presence of oxygen, the cathodic current at the electrode, which is diffusion limited, will be expected to increase as observed, without the production of any other organic product of **III** (except the anion radical).

Figure 3 shows a plot of the normalized (to the square root of the sweep rate) current magnitude as a function of the sweep rate for the aromatic hydrocarbon-oxygen system. The lowest plot (I) is that for the oxygen reduction peak. Plot II is that for the uncomplicated one electron reduction peak of **III** to its anion radical in the absence of oxygen. Plot III is for the cathodic peak at -2.35 V when both **III** and oxygen are present in comparable amounts. The reduction peak in plot III is the sum of the currents for the reduction of **III** to its anion radical and the reduction of electroactive products formed from the reaction of the anion radical with oxygen and superoxide, which the data suggest to be more regenerated **III** as proposed in the preceding paragraph.

It should be noted that in the mixed system, a subsequent cathodic excursion following cyclic voltammetry from 0 to -2.5 V vs. Ag/Ag⁺ gave rise to no additional reduction waves at lower potentials than that for **III** reduction. This is further evidence that no long-lived organic products of the reaction of the anion radical with O_2 and superoxide other than **III** are generated. Though short-lived products of this reaction cannot be ruled out, the fact that the cathodic peak at -2.35 V grows in comparison with the anodic peak at -2.29 V is certainly consistent with regeneration of additional **III**.

The half wave potential for the reduction of **III** is 400 mV more negative than that for the reduction of **V** (5). This is the expected result in view of the greater delocalization of the extra electron possible in the larger π orbital system: the stability of the naphthyl anion is greater than that of the benzyl analog, just as it is known to be in naphthalene and benzene. We have performed simple Hückel calculations on **III** and **V** and find that this assumption is in line with the results of those calculations.

B. Cations

In deoxygenated acetonitrile solution, a voltammetric sweep to positive potentials gives rise to single electron oxidations of **III** to its radical cation and of its radical cation to dication (Fig. 4). The second reduction is irreversible: the lifetime of the dication is very short on the experimental timescale. On the other hand, the anodic and cathodic peak potential separation (corresponding to oxidation of **III** and reduction of III^{*+} , respectively), approach 60 mV when sweep rates are increased to 500 mV s⁻¹, suggesting electrochemical reversibility at this sweep rate; the half-wave potential there is $+0.68$ V. However, up to 500 mV s⁻¹, the anodic peak current (oxidation of **III**) is greater than the cathodic peak current (reduction of III^{*+}), and the ratio of cathodic to anodic peak current increases with sweep

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rate (Fig. 5). These observations are consistent with a reversible electron transfer followed by kinetic decomposition of the resulting cation radical (5). If the potential is swept immediately to more negative values following the oxidation of III to its cation radical, a new peak appears at about -0.7 V (Fig. 4), this peak is due to the reduction of protons formed in the decomposition of the cation radical. If the potential is swept positive enough to form the dication, and then immediately swept negative to potentials where the anion radical is formed, no peak for the reduction of the dication is observed; only the reduction due to the protons is evident.

At a glassy carbon electrode, virtually identical behavior was observed for III at all applied potentials except the cathodic peak at -0.7 V disappeared, which confirms that this wave corresponds to the reduction of protons formed in the first anodic wave. Also, oxygen had no effect on the electrochemistry of the cation radical or dication; the very same voltammetry as described above was observed even if oxygen was present in solution.

It is interesting to note that the half wave potential for the oxidation of the benzyl derivative III is about 130 mV less positive than the half wave potential for the oxidation of the naphthyl derivative V (5). This surprising result is not explained by simply considering the stabilities of the ions as was possible in the case of the reduction of these two compounds. The result can be explained for both oxidation and reduction if one assumes that there is a large difference in the ground state energies of the two neutral compounds III and V, and lesser differences in the electronic energies of their respective cation radicals. If neutral V is energetically more stable than III, it will be more difficult to oxidize than III, given that the cations of each are closer in energy than are the neutral species. This trend was indeed indicated in the Hückel calculations; the overall stabilization energy of V was predicted to be greater than that of III, whereas the electronic energy difference between the cation radicals is less than the energy difference between the neutral species.

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C. Structural considerations

The consideration of the possible structures of the electrochemically formed ion radicals is of interest. The reversible behavior of **III** upon oxidation and reduction indicates that no opening of the three-membered ring occurs when either the cation radical or the anion radical is formed. The compound is reduced at slightly less negative potentials than many other aromatic hydrocarbons in acetonitrile. The half-wave potential for the reduction of **III** was seen to be -2.32 V vs. Ag/Ag^+ . This value compares with half-wave potentials of -2.9 V for naphthalene, -2.5 V for tetraphenylethylene, -2.5 V for pyrene, -2.4 V for diphenylanthracene, and -1.93 V for diphenylmethylenecyclopropa[*b*]naphthalene. Compound **III** is oxidized at somewhat less positive potentials than many other aromatic hydrocarbons in this solvent. It has a half-wave potential of $+0.68$ V for oxidation to the cation radical. For naphthalene this value is $+1.40$ V, for pyrene $+1.06$ V, for tetraphenylethylene $+1.0$ V, for diphenylanthracene $+0.92$ V, for anthracene $+0.91$ V, for diphenylmethylenecyclopropa[*b*]naphthalene $+0.81$ V, and for perylene $+0.66$ V.³

On formation of the radical ions, it is most likely that the olefinic double bond is broken. This release of strain would yield a reduced free energy of ion formation. The anion would be then formed at less negative potentials and the cation formed at less positive potentials than what might be predicted from half-wave potentials of other aromatic hydrocarbons. Proposed structures for the anion radical are:

while possible structures for the radical cation might be:

It is not possible from our voltammetric data to conclude for either species which resonance structure contributes most to the lowest overall energy state.

Spectroelectrochemistry

A. The anion radical

Modulated specular reflectance spectroscopy (MSRS) in the visible range was performed on solutions containing **III** (1 mM) in acetonitrile in the absence of oxygen. The potential was stepped from 0 to -2.50 V and the frequency of modulation was 40 Hz. The MSRS technique is described more explicitly in refs. 8 and 12. A single peak ($\lambda_{\text{max}} = 587$ nm) due to absorption by the radical anion was observed. Reflection spectroelectrochemical transients for the formation of the anion radical were then obtained at this wavelength using the same potentials. Figure 6 shows the transient for radical anion formation of **III** at the platinum mirror electrode in the absence of oxygen. Composite transient data from 100 , 200 , 400 , and 1000 ms transients were combined to examine the linearity of the optical response with the square root of time over an extended period. Linearity indicates anion radical stability over the examined timescale, if the amplitude of $\Delta R/R$ is kept small. The plots of $-\Delta R/R$ vs. $t^{1/2}$ were indeed linear with a correlation coefficient of 0.99885 , showing the radical anion to be very stable for times of at least 1 s. This also demonstrates the reproducibility and accuracy of this transient technique.

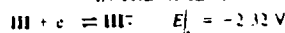
Figure 7 shows the transient that results when oxygen is present in solution together with **III**. MSRS data of this system at the same potentials of modulation still revealed a single peak at the same wavelength as that for the oxygen-free system, demonstrating that superoxide does not absorb at this or at any nearby frequency. We still observe the formation of the radical anion during the forward potential step although the reflectance is somewhat less. When the potential is reversed to its base value, however, to where only neutral **III** and O_2 are stable, the reflectance, which is proportional to absorbance at low values of $\Delta R/R$, is observed to decay rapidly to zero. Clearly, the anion radical of **III** reacts rapidly with oxygen.

Regeneration of **III** is suggested by the observed reflectance-time profile during the forward applied potential pulse; the shape of the transient is still a linear function of the square root of time. $\text{III}^{\cdot-}$ diffuses from the electrode surface into the oxygen and superoxide rich solution, neutral **III** is formed and can therefore diffuse back to the electrode and undergo another reduction.

The results are consistent with the following proposed

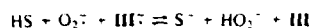
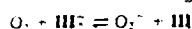
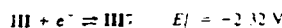
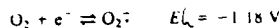
mechanism for the cathodic reduction of III

IN THE ABSENCE OF OXYGEN



In oxygen-free solution a simple electron transfer occurs reversibly to form the anion radical from neutral III.

IN THE PRESENCE OF OXYGEN



Here the mean of the oxidation and reduction peak potentials for dioxygen have been taken to be the standard potential. During the forward potential step, the rate of production of the anion at the electrode is limited by the diffusion of the neutral species to the surface. Reaction of anion with oxygen and superoxide regenerates the neutral molecule, so more of III is available to diffuse to the interface. Because of this, the absorbance of the radical anion in oxygen-containing solution is not much lower than it is in the solution in which oxygen is not present. During the reverse potential pulse, however, the oxygen consumes the anion while the regenerated starting material cannot react electrochemically to form more anion to replace that which is consumed. The reflectance therefore falls rapidly in comparison to the case in an oxygen-free environment.

The supporting electrolyte cation, TBA^+ , probably acts as a proton donor in the proposed scheme. The peroxide dianion most likely abstracts a proton from the background electrolyte. Further studies on this possibility are underway and will appear elsewhere.

Evidence for the greater stability of the anion radical of V than that of III is apparent from the MSRS experiment. The wavelength of maximum absorption for the anion radical of III appears at 587 nm, while that for the anion radical of V is observed at 529 nm (5); the energy of the electronic transition for the naphthyl derivative anion radical is higher than that for the benzyl derivative anion radical. Energy levels predicted from the Hückel calculations appeared at relative energies which are consistent with these data.

B. The cation radical

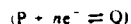
A reflectance transient spectrum was obtained as before for the cation radical formation from III, by stepping the electrode potential (chronoamperometric experiment) from 0 to +0.9 V, which causes diffusion-controlled mass transport of neutral III to the electrode. The current response indicated a simple one-electron transfer. The wavelength of maximum $\Delta R/R$ was found at 473 nm for the formation of the radical cation. Identical spectra resulted whether O_2 was present or absent in the solution. Spectroelectrochemical transients for the anodic oxidation of III to its radical cation were then taken at the above λ_{max} for pulse lengths of 10, 40, 100, 200, and 400 ms duration; a typical transient is shown in Fig. 8. Such transients were identical whether O_2 existed in solution or did not, suggesting no cation radical reaction with oxygen. The composite data from the above transients of different length were plotted as before ($\Delta R/R$ vs. $t^{1/2}$) (Fig. 9). The plot is linear up to times of about 100 ms, and thereafter we see a fall-off region; the cation radical is stable for a short period before it undergoes decay.

Whether this decay involves an electron transfer or not, a chemical step is certainly involved; it is the product of this decay which appears at cathodic potentials upon reverse sweep to negative values in the cyclic voltammetry described earlier. Assuming first or pseudo first order kinetic behavior, we can compute the homogeneous rate constant for the decay of the radical cation from the spectroelectrochemical data utilizing the technique described in refs. 12 and 13, where the rate constant

$$k = \frac{\left[-\frac{\Delta R}{R} \right]_0 - \left[-\frac{\Delta R}{R} \right]_t}{\int_0^t \left[-\frac{\Delta R}{R} \right] dt}$$

Here $[-\Delta R/R]_0$ is the change in reflectance which would be obtained at time t if the absorbing species does not decay, and $[-\Delta R/R]_t$ is the change in reflectance where decay occurs with a first order rate constant k . Computation of this k value was performed from data from various transients in excess of 100 ms length, and a mean homogeneous first order rate constant of 1.99 s^{-1} was determined for the degradation of the cation radical.

The data are consistent with the following mechanism for the oxidation of III, either in the presence or absence of oxygen:



It was not possible from the spectroelectrochemical data to determine between an EC or an ECE mechanism where the second electron transfer could not be observed (*vide infra*).

The electrochemical and spectroelectrochemical (*vide infra*) evidence is for an EC type of reaction mechanism: subsequent electron transfer reactions are not indicated after the initial chemical reaction product is formed. If the concentration of the hydrocarbon is increased, the rate constant for reaction of the cation radical does not increase when the solution is very dry, indicating that in this solvent of low nucleophilicity, dehydrodimerization reactions to form the biphenyl or other dimer products with starting material or other cation radicals is not the major chemical reaction of the cation radical. The reaction also is not dependent on the nature or concentration of supporting electrolyte as long as the solutions are of sufficient conductivity to allow for reliable electrochemical measurements; lithium perchlorate, tetrabutylammonium tetrafluoroborate, and tetraethylammonium perchlorate all gave similar results at 0.05, 0.10, and 0.25 M concentrations. Water addition at the 1–20 mM level in all of these solutions did not lead to changes in the rate of cation radical reaction.

Other possible pathways (13, 15) for hydrocarbon cation radical reactions are well known. They proceed generally by an ECE type reaction, such as loss of proton to give the free radical with subsequent loss of another electron to give the carbenium species, which reacts with any nucleophile to give stable products. Disproportionation reactions occur much less frequently, and these are also overall two electron transfer reactions. The most plausible reaction is that there is a proton loss (*vide supra*) to form the free radical of III, which is (a) either electrochemically more difficult to oxidize than the starting material (this is indicated by the Hückel calculation), and/or (b) because of the slow rate of production from the cation the free radical species will be concentrated at a distance far from the electrode compared to the size of the reaction layer of the radical. The radical reacts away (probably by radical–radical dimerization) before it can be transported back to the electrode to undergo another electron transfer (cf. (a)).

MSRS spectra for the cation radicals of III and V gave similar wavelengths of maximum absorption: 473 and 480 nm, respectively. This indicates that the cation radicals have similar ground state electronic energies. The HOMO–LUMO electronic transition energies calculated with the Hückel programs were also consistent with these observations.

Conclusion

The voltammetric and spectroelectrochemical studies of the title compound suggest significant electronic differences in both III and V as well as their respective anion radicals, while indicating that the cation radicals of the two species are energetically similar. Studies on neutral alkylidene cyclopropenes (14) have shown the stability of the cyclopropabenzene derivatives to be less than that of their naphthyl homologs. Simple Hückel molecular orbital calculations gave results which were consistent with these observations.

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2C

FIG. 1. Cyclic voltammetry for (a) 1 mM **III** and for (b) dioxygen in 0.15 M TBAF/acetonitrile solution at a platinum electrode. The sweep rate was 50 mV s⁻¹. Potentials are vs. the Ag/Ag⁺ (0.01 M AgNO₃ in 0.1 M TBAF in acetonitrile) reference electrode.

FIG. 2. Cyclic voltammetry of the mixed system of the components in Fig. 1. Parameters the same as in Fig. 1.

FIG. 3. Plots of the normalized peak current vs. sweep rate for the data in Figs. 1 and 2. (I) is that for the reduction peak in Fig. 1b; (II) is that for the reduction peak in Fig. 1a; (III) is for the reduction peak at -2.35 V in Fig. 2. Except for the sweep rate, the parameters are the same as those in Fig. 1.

FIG. 4. Cyclic voltammetry of 1 mM **III** in acetonitrile. Potential program was 0.0 V to positive potentials, then reversing to negative potentials, then returning to zero. Parameters the same as in Fig. 1.

FIG. 5. Cyclic voltammetry of 1 mM **III** in acetonitrile as a function of sweep rate. Parameters the same as in Fig. 1.

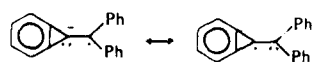
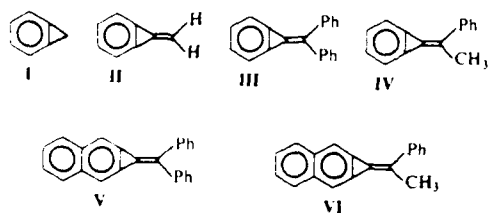
FIG. 6. Reflectance spectroelectrochemical transient at 583 nm for the anion radical of **III** in the solution described in Fig. 1a. (The solution is oxygen-free.)

FIG. 7. Reflectance spectroelectrochemical transient at 587 nm for the anion radical of **III** in the solution described in Fig. 2. (The solution contains oxygen.)

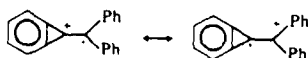
FIG. 8. Reflectance spectroelectrochemical transient at 473 nm for the cation radical of **III** in the solution described in Fig. 4.

FIG. 9. Reflectance vs. square root of time plot for the formation of the cation radical from transients of duration: +, 20 ms; □, 40 ms; ◇, 100 ms; ×, 200 ms; ○, 400 ms. Solution is that described in Fig. 4.

—END OF FILE 2—



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